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SULFONATION OF F-BUTYL F-VINYLETHER: SYNTHESIS OF A NEW FLUORINATED β-SULTONE AND DERIVATIVES

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SUMMARY

The new fluorinated β-sultone, $CF_3(CF_2)_3O\overline{CFCF_2SO_2O}$ (I) has been prepared from F-butyl F-vinyl ether and sulfur trioxide. It isomerizes to $CF_3(CF_2)_3OC(O)CF_2SO_2F$ (II) when heated with sodium fluoride.

Two known fluorinated esters, $FSO_2CF_2C(O)OCH_3$ (III) and $CF_3(CF_2)_2C(O)OCH_3$ (IV), have also been synthesized from the reaction of methanol with the β-sultone (I).

INTRODUCTION

Fluorinated β-sultones are an important class of compounds which lead to derivatives containing the fluorosulfonyl grouping (SO_2F). It is known that incorporating this group into a molecular system can lead to the production of compounds useful as ion-exchange resins, surface active agents and strong sulfonic acids [1-4]. Previously, we reported that the reaction of $R_fOCF_2CF{=}CF_2$ with SO_3 gave the corresponding sultones [5]:

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$$R_fOCF_2CF{=}CF_2 + SO_3 \xrightarrow{\Delta} R_fOCF_2\overline{CFCF_2OSO_2} \quad (1)$$

where R_f = CF_3 and $CF_3OCF_2CF_2$. In this case, the electrophilic addition of SO_3 to the F-alkyl F-allyl ethers occurred in the expected fashion:

$$SO_3 + R_fOCF_2CF{=}CF_2 \longrightarrow R_fOCF_2\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle O_2SO^-}{|}}{C}}CF_2^+ \longrightarrow R_fOCF_2\overline{CFCF_2OSO_2}$$

However, with $R_fOCF{=}CF_2$ the reverse direction of addition is found. To date only a few reactions of F-alkyl F-vinyl ethers with SO_3 have been studied [6-8]. In our continuing studies of fluoro β-sultones, we wish to report our results with $CF_3(CF_2)_3OCF{=}CF_2$ to prepare a new perfluoro β-sultone, $CF_3(CF_2)_3O\overline{CFCF_2SO_2O}$ (I), and its rearranged isomer, $CF_3(CF_2)_3OC(O)CF_2SO_2F$ (II). The reaction of β-sultone (I) with CH_3OH is also reported.

RESULTS AND DISCUSSION

The following new fluoro β-sultone was produced via the reaction of $CF_3(CF_2)_3OCF{=}CF_2$ with monomeric sulfur trioxide in a modified Carius tube under autogenous pressure at a temperature greater than 100°C.

$$CF_3(CF_2)_3OCF{=}CF_2 + SO_3 \xrightarrow{\Delta} \underset{\text{I}}{CF_3(CF_2)_3O\overline{CFCF_2SO_2O}} \quad (2)$$

In the above reaction, the product formed by the cycloaddition reaction of the alkene with sulfur trioxide occurred in a reverse order; apparently the incorporation of the unpaired electron from the ether oxygen into the electron cloud of the π-olefinic system creates a conjugated system in which the olefinic carbon of the CF_2 group has a partial negative charge and bonds with the sulfur portion of the SO_3 [5,6,10].

Treatment of the β-sultone (I) with sodium fluoride produced the corresponding isomeric fluorosulfonyl ester:

$$\mathrm{I} \xrightarrow[\Delta]{NaF} \underset{\mathrm{II}}{CF_3(CF_2)_3OC(O)CF_2SO_2F} \tag{3}$$

The new fluoro β-sultone (I) reacts with an excess amount of cold methanol according to the following equation:

$$\mathrm{I} + CH_3OH \xrightarrow{\text{ice bath}} \underset{\mathrm{III}}{FSO_2CF_2C(O)OCH_3} + \underset{\mathrm{IV}}{CF_3(CF_2)_2C(O)OCH_3} \tag{4}$$

A possible reaction pathway for the reaction (4) is:

$$CF_3(CF_2)_3O\overline{CFCF_2SO_2O} + \text{xs. } CH_3OH \longrightarrow CF_3(CF_2)_3O\overset{{}^-O}{\overset{|}{C}}F\text{-}\underset{\underset{\underset{CH_3O^+H}{|}}{SO_2}}{\underset{|}{CF_2}} \tag{4a}$$

$$CF_3(CF_2)_3O\overset{{}^-O}{\overset{|}{C}}\text{-}\underset{\underset{\underset{CH_3O^+H}{|}}{F\;SO_2}}{\underset{|}{CF_2}} \longrightarrow CF_3(CF_2)_3OC(O)CF_2SO_2F + CH_3OH \tag{4b}$$

$$CF_3(CF_2)_3OC(O)CF_2SO_2F + CH_3OH \longrightarrow$$

$$FSO_2CF_2C(O)OCH_3 + [CF_3(CF_2)_2CF_2O^- + H^+] \tag{4c}$$

$$[CF_3(CF_2)_2CF_2O^- + H^+] \longrightarrow CF_3(CF_2)_2C(O)F + HF \quad (4d)$$

$$CF_3(CF_2)_2C(O)F + CH_3OH \longrightarrow CF_3(CF_2)_2C(O)OCH_3 + HF \quad (4e)$$

The resulting two esters are thermally stable and colorless liquids.

The infrared spectra of the new compounds have several common features. The compounds I and II contain the asymmetric and symmetric SO_2 stretching vibration at 1497-1449 and 1260-1218 cm^{-1}, respectively; these values are in good agreement with other fluorinated β-sultones and their derivatives [3,4,5,9]. The carbonyl stretching vibration for compound II is found in the 1845 cm^{-1} region. The carbon-fluorine vibrational bands are located in the 1346-1114 cm^{-1} region. The sulfur-fluorine stretching vibration of the fluorosulfonyl group in compound II is found near 800 cm^{-1}. In all cases these assignments are in excellent agreement with literature values [3,4,5,9].

The major mass spectral peaks for new compounds I and II are listed in the experimental section. The molecular ions were not observed for these compounds while MH^+ peaks were found for both of them. Additional $M\text{-}X^+$ or $MH\text{-}X^+$ peaks, such as $M\text{-}C_4F_9^+$, $M\text{-}CF_2SO_2F^+$, $MH\text{-}SO_3^+$, $MH\text{-}O^+$ were also found.

The ^{19}F nmr chemical shift values and coupling constants are given in the experimental section. Resonances for the nonequivalent CF_2 fluorines in the β-sultone (I) are found in the -84.2 to -87.0 ppm range; for other similar sultones, $CF_3(CF_2)_2O\overline{CFCF_2SO_2O}$ and $C_2H_5O\overline{C(CF_3)CF_2SO_2O}$, CF_2 resonance bands are located in the -84.1 to -100.5 ppm range [6]. Generally the range for nonequivalent fluorines of the CF_2 group in the sultone ring is reported between -72.8 to -89.5 ppm [3,4,5,9,11].

The ^{19}F nmr values for the following functional groupings $\underline{CF_3}$-, $CF_3\underline{(CF_2)_2}$, $\underline{CF}$, $\underline{CF_2}O$ (AB pattern in the case of β-sultone), $\underline{CF_2}SO_2F$, and $\underline{SO_2}F$ in compounds I and II are all in excellent agreement with literature values [4-6,9,10].

EXPERIMENTAL

The F-vinyl ether, $CF_3(CF_2)_2CF_2OCF=CF_2$, was supplied by 3M Company. All other chemicals were obtained from commercial sources and used as received.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex-glass cell with KBr windows or as liquids between KBr disks on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for the fluorine resonance. $(CH_3)_4Si$ and $CFCl_3$ were used as external standards. The purities of compounds I and II were also checked via gas chromatography using an Aerograph autoprep (model A-700) gas chromatograph. Mass spectra were taken on a VG-7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluoro-kerosene was used as an internal standard.

Elemental analyses were performed by the Beller Microanalytical Laboratory in Göttingen, Federal Republic of Germany.

Synthesis of $CF_3(CF_2)_2CF_2O\overline{CFCF_2SO_2O}$

To 40 mmol of SO_3 in a 130 mL Pyrex-glass Carius tube, equipped with a Kontes Teflon valve, 19.9 mmol of $CF_3(CF_2)_2CF_2OCF{=}CF_2$ was added. The mixture was heated at 105±5°C for 7 days. Distillation of the mixture gave 8.84 mmol of a clear liquid, $CF_3(CF_2)_2CF_2O\overline{CFCF_2SO_2O}$, in 44.4% yield, b.p. 85-90°C/197 mm.

The infrared spectrum had the following bands (cm^{-1}): 1473(m), 1449(vs), 1346(ms), 1307(vs), 1260(vs), 1221(s), 1199(sh), 1152(s), 1144(sh), 1125(sh), 1112(w), 1088(vw), 1059(ms), 1027(s), 997(w), 995(m), 936(w), 924(vw), 896(ms), 821(m), 779(m), 742(s), 717(vw), 701(vw), 666(w), 634(w), 604(sh), 594(w), 573(vw), 538(vw), 534(w), 484(m), 459(w), 443(w), 437(w), 418(w), 406(w).

The ^{19}F nmr contained the following peaks (ppm): CF_3 (-84.5, triplet, 3.0), $CF_{2AB}(SO_2)$ [(A branch, -84.2, doublet of multiplet, 1.0)(B branch, -87.0, doublet of multiplet, 1.0), $J_{A,B}$ = 153.3 Hz], CF (-91.8, multiplet, 1.0), $CF_{2AB}O$ [(A branch, -100.6, doublet of multiplet, 1.0)(B branch, -102.8 doublet of multiplet, 0.8) $J_{A,B}$ = 158.1 Hz], and $(CF_2)_2$ (-129.5, multiplet, 4.5).

The positive ion $(CI)^+$ mass spectrum (m/e species): 397, MH^+; 316, $(M\text{-}SO_3)^+$; 263, $(M\text{-}CF_2SO_2F)^+$; 225, $C_4F_7OC(O)^+$; 219, $C_4F_9^+$; 197, $C_3F_7CO^+$; 181, $C_3F_7C^+$; 177, $OCF(O)CF_2SO_2^+$; 170, $CF_2OC(O)CSO_2^+$; 169, $C_3F_7^+$; 161, $CF(O)CF_2SO_2^+$; 155, $C_4OCCFSO^+$; 151, $COCF(O)CSO_2^+$; 150 $C_3F_6^+$; 131, $C_3F_5^+$; 119, $C_2F_5^+$; 113, $CFCF_2S^+$ or $OCF(O)CF_2^+$; 100, $C_2F_4^+$; 99, $C_2OCF(O)C^+$; 98, CF_2SO^+; 97, $OCFCF_2^+$; 95, $CFSO_2^+$; 93, CF_3CC^+; 87, $CFOC(O)C^+$; 83, $CFCCCO^+$; 81, CF_2CF^+; 78, CF_2CO^+; 75, $OCF(O)C^+$; 71, $CFOCC^+$; 69, CF_3^+; 64, SO_2^+; 63, CFS^+; 59, $OCFC^+$.

Anal. calcd for $C_6F_{12}O_4S$: C, 18.19; F, 57.60; S, 8.09. Found: C, 17.82; F, 57.10; S, 8.27%.

Synthesis of $CF_3(CF_2)_2CF_2OC(O)CF_2SO_2F$

To a 25 ml Pyrex-glass round-bottom flask, equipped with a Teflon-coated stirring bar, were added 5.7 mmol of dry NaF, and 7.1 mmol of $CF_3(CF_2)_2CF_2O\overline{CFCF_2SO_2O}$. The reaction vessel was connected to a trap cooled to -78°C through a reflux condenser. The reaction mixture was heated to 65±5°C for 4 days. Distillation of the mixture gave 2.4 mmol of a colorless liquid, $CF_3(CF_2)_2CF_2OC(O)CF_2SO_2F$, in 33.7% yield; b.p. 55±1°C/600 μ.

The infrared spectrum had the following bands (cm^{-1}): 1845 (s), 1835 (sh), 1837 (s), 1497 (s), 1488 (sh), 1473 (vw), 1476 (s), 1418 (vw), 1391 (vw), 1302 (s), 1242 (sh), 1218 (vs), 1156 (vw), 1144 (s), 1111 (s), 1062 (ms), 991 (m), 975 (m), 949 (w), 934 (vw), 924 (vw), 895 (ms), 857 (m), 812 (sh), 797 (s), 787 (s), 762 (w), 740 (m), 723 (vw), 709 (vw), 697 (w), 685 (sh), 667 (w), 648 (sh), 637 (w), 625 (w), 613 (sh), 599 (vw), 587 (m), 575 (w), 560 (m), 548 (m), 534 (m), 522 (m), 510 (vw), 498 (vw), 483 (vw), 461 (vw), 438 (w), 426 (w), 412 (ms).

The ^{19}F nmr contained the following peaks (ppm): FSO_2 (50.0, broad singlet, 0.8), CF_3 (-83.7, triplet, 2.9, J_{CF_2,CF_3} = 9.2 Hz), CF_2O (-88.3, multiplet, 1.8, J_{CF_2,CF_2} = 10.6 Hz), $C(O)CF_2$ (-103.7, doublet, 2.1, J_{FSO_2,CF_2} = 2.1 Hz), and $(CF_2)_2$ (129.2, multiplet, 3.8).

The positive ion $(CI)^+$ mass spectrum (m/e): 397, MH^+; 381, $(MH\text{-}O)^+$; 313, $(M\text{-}SO_2F)^+$; 263, $(M\text{-}CF_2SO_2F)^+$; 220, $(MH\text{-}OCOCF_2SO_2F)^+$; 219, $C_4F_9^+$; 213, $C_3F_7OCO^+$; 177, $(M\text{-}C_4F_9)^+$; 169, $C_3F_7^+$; 161, $(M\text{-}C_4F_9O)^+$; 119, $C_2F_5^+$; 100, $C_2F_4^+$; 95, CSO_2F^+; 94, $OC(O)CF_2^+$; 83, SO_2F^+; 79, $CSOF^+$; 75, $OC(O)CF^+$; 69, CF_3^+; 67, SOF^+; 64, SO_2^+; 56, $OCOC^+$.

Anal. Calcd for $C_6F_{12}O_4S$: C, 18.19; F, 57.60; S, 8.09. Found: C, 17.95; F, 57.1; S, 7.96%.

Synthesis of $CH_3OC(O)CF_2SO_2F$ and $CH_3OC(O)C_3F_7$

To 53.8 mmol CH_3OH at 0°C in a 25 ml Pyrex-glass round-bottom flask, equipped with a Teflon-coated stirring bar, 4.8 mmol of $CF_3(CF_2)_2CF_2O\overline{CFCF_2SO_2O}$ was added over a period of 15 min. The reaction mixture was warmed to 25°C, washed with cold water and dried over $MgSO_4$. Distillation of the mixture gave 0.48 mmol of a colorless liquid, $CH_3OC(O)C_3F_7$, in 10.1% yield; b.p. 59-64°C and 0.68 mmol of another colorless liquid, $CH_3OC(O)CF_2SO_2F$, in 14.2% yield; b.p. 55±1°C/166 mm. The infrared spectrum, of $CH_3OC(O)CF_2SO_2F$, agrees with that previously reported [12].

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